PATENT SPECIFICATION

NO DRAWINGS

Inventor: NEIL HUNTER RAY

905,006

Date of filing Complete Specification: Oct. 26, 1960.

Application Date: Nov. 24, 1959. *No. 39907/59.*

Complete Specification Published: Sept. 5, 1962.

Index at acceptance:—Classes 2(3), C1C(4:5:7B:8:11J); and 2(6), P7(D1A:K11), P10(D1A:K11), P11D2X, P11K(7:10).

International Classification:—C07c. C08f.

COMPLETE SPECIFICATION

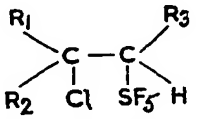
Unsaturated Compounds containing the Pentafluorothio Group

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company. do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel unsaturated organic compounds containing the pentafluorothio group —SF_5 and to a method of making them.

It is well known in organic chemistry to make unsaturated compounds containing the >C=C< group by removal of the elements of a halogen acid from a saturated compound by means of alcoholic or aqueous alcoholic solutions of caustic potash or caustic soda, where the halogen is chlorine, bromine or iodine. This process is not readily applicable to fluorinated compounds, for one reason because it is usually not possible to obtain the necessary intermediate compound containing the proper number of fluorine atoms.

In co-pending application No. 31208/59 Serial No. 891,552 we have described a method for preparing compounds having the general formula

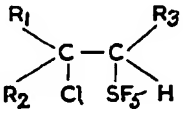


by adding sulphur chloride pentafluoride, SF_5Cl, across the double bond of an olefine or other non-aromatic compound containing the ethylenically unsaturated group >C=C<. In this formula R_1 is hydrogen or chlorine, R_2 is hydrogen or an alkyl group or an alkenyl group, R_3 is hydrogen, or R_2, R_3 are joined in a cycloalkyl ring. Since sulphur chloride pentafluoride is very readily hydrolysed by alkali it was expected that compounds having this general formula would on treatment with alcoholic or aqueous alcoholic caustic potash or caustic soda lose all the —SF_5 group. For example we should have expected

$$CH_2Cl—CH_2SF_5,$$

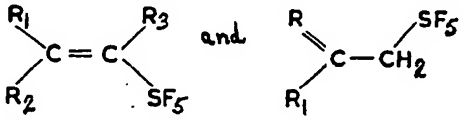
obtained by adding SF_5Cl to ethylene to yield vinyl chloride, potassium sulphate and potassium fluoride on treatment with caustic potash. Surprisingly we have found that under such conditions the —SF_5 group is not attacked but instead the elements of hydrochloric acid are removed and new unsaturated compounds containing the —SF_5 group are formed.

According to our invention we provide new unsaturated organic compounds containing the pentafluorothio group —SF_5, and a process for making them comprising removing the elements of hydrogen chloride from the addition products obtained by adding sulphur chloride pentafluoride to olefines and other non-aromatic ethylenically unsaturated compounds, said addition products having the general formula



in which R_1, R_2, and R_3 have the meanings hereinbefore defined.

The new compounds of our invention have structures of the general types represented by



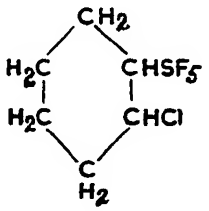
where R_1, R_2, and R_3 have the meanings hereinbefore defined, and R is the alkylidene or alkenylidene radical derived from the original alkyl or alkenyl radical R_2. The structure-type depends on which carbon atom of the sulphur chloride pentafluoride/olefine addition product loses a hydrogen atom in the dehydrochlorination. For example, if in the addition product only hydrogen, or hydrogen and halogen atoms are attached to the two carbon atoms of the original ethylenic bond the new compounds are of type I. Thus ethylene gives the addition product 2-chloroethyl sulphur pentafluoride

$$CH_2Cl—CH_2SF_5$$

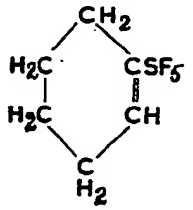
which then gives the new compound vinyl sulphur pentafluoride

$$CH_2=CH.SF_5.$$

Likewise cyclohexene gives first 1-chlorocyclohexyl sulphur pentafluoride



which then gives cyclohexenyl sulphur pentafluoride on dehydrochlorination



Vinyl chloride gives the additive product 2,2-dichloroethyl sulphur pentafluoride

$$CHCl_2—CH_2.SF_5$$

which by dehydrochlorination gives 2-chlorovinyl sulphur pentafluoride

$$CHCl=CH.SF_5,$$

and likewise trifluoroethylene gives 1H.2-chlorotrifluoroethyl sulphur pentafluoride

$$CF_2Cl—CHF.SF_5$$

from which perfluorovinyl sulphur pentafluoride

$$CF_2=CF.SF_5$$

is made by dehydrochlorination.

On the other hand, if in the sulphur chloride pentafluoride/olefine addition product one or more alkyl groups is attached to either or both of the carbon atoms of the original ethylenic bond the hydrogen atom lost in the dehydrochlorination may come from a carbon atom in the α position to the original ethylenic carbon atoms and then new compounds of type II will be formed. For example, propylene gives the addition product 2-chloropropyl sulphur pentafluoride

$$CH_3.CHCl.CH_2.SF_5$$

which on dehydrochlorination gives allyl sulphur pentafluoride

$$CH_2=CH.CH_2.SF_5$$

as well as propenyl sulphur pentafluoride

$$CH_3—CH=CH.SF_5.$$

The method of making the new compounds is essentially to remove the elements of hydrogen chloride from the olefine/sulphur chloride pentafluoride addition compounds by refluxing them with an alcoholic or aqueous-alcoholic solution of caustic soda or caustic potash containing 10—25% of the latter for half an hour or more. A suspension of finely divided caustic soda or potash in a non-aqueous inert organic solvent, for example petroleum ether, may be used if desired in place of the solution. The reflux condenser exit may be connected to a cold trap if the more volatile compounds are being made. For the less volatile compounds the reaction mixture after refluxing may be poured into water and the product extracted with ether and the extract distilled.

The new compounds are reactive intermediates for introducing —SF_5 groups into other molecules and are also monomers for polymerisation and copolymerisation. For example vinyl sulphur pentafluoride copolymerises with ethylene, and with vinyl chloride. The copolymers with ethylene, for example 1:6 and 1:3 moles vinyl sulphur pentafluoride/moles ethylene, are more flexible and more transparent than normal polythene.

The following examples illustrate but do not limit the invention.

EXAMPLE 1.

Potassium hydroxide (19 g.) was dissolved in water (20 cc.) and alcohol (60 cc.) was added. This solution was boiled under a reflux condenser to the top of which was connected a trap cooled in a solid carbon dioxide/alcohol freezing mixture. While the solution was boiling 2-chloroethyl sulphur pentafluoride (33 g.; prepared from ethylene and sulphur chloride